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*ELECTROLYTIC REMOVAL OF NITRATE FROM CELSS CROP RESIDUES*

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## ABSTRACT

The CELSS resource recovery system, which is a waste processing system, uses aerobic and anaerobic bioreactors to recover plants nutrients and secondary foods from the inedible biomass. Studies have been carried out using aerobic and anaerobic bioreactors to recover plants nutrients and secondary foods from inedible crop residues. Crop residues contain significant amount of nitrate. There are actually two major problems concerning nitrate: 1) both CELSS biomass production and resource recovery consume large quantities of nitric acid, 2) nitrate causes a variety of problems in both aerobic and anaerobic bioreactors. Previous studies with aerobic biodegradation have experienced nitrogen losses through denitrification when low level of dissolved oxygen are reached due the rapid organic matter degradation. During the anaerobic biodegradation of inedible biomass, nitrate is converted to ammonia which reduces the system capacity to convert the organic matter to volatile fatty acids and needs further downstream processing steps to convert the ammonia back to nitrate. The nitrate anion causes several problems in the resource recovery system in such a way that, removal prior to the process is highly desirable.

The technique proposed to remove the nitrate from potato inedible biomass leachate and to satisfy the nitric acid demand was a four compartment electrolytic cell. In order to establish the electrolytic cell performance variables, a series of experiments were carried out using potato crop residues aqueous leachate as the diluate solution. The variables studied were the potato biomass leachate composition and electrical properties, preparation of compartment solutions to be compatible with the electrolytic system, limiting current density, nutrients removal rates as a function of current density, fluid hydrodynamic conditions, applied voltage, and process operating time during batch-recirculation operation.

Results indicated that the limiting current density (maximum operating current density) was directly proportional the solution electrical conductivity an a power function of the linear fluid velocity in the range between 0.083 to 0.403 m/s. During the electrolytic cell once-through operation, the nitrate, potassium, and other nutrients removal rates were proportional to the current density and inversely proportional to fluid velocity. The removal of monovalent ions was found to be higher than divalent ones. Under batch-recirculation operation at constant applied voltage of 4.5 and 8.5 volts, it was found that the nutrient removal rates were independent of applied voltage, but proportional to the ions concentration and operating time. From material balances it was found that 2.2 moles of oxygen gas and 4.4 moles of hydrogen gas were produced at the electrodes surfaces per mole of nitrate transferred.

## SUMMARY

The National Aeronautical and Space Administration (NASA) has been studying the viability of Controlled Ecological Life Support System (CELSS) for long term space missions for several years. The purpose of this system is to provide all the basic human needs required for life support. The CELSS breadboard project is a large-scale integration system with two main components, a full-scale Biomass Production Chamber (BPC) and the Resource Recovery system. The BPC is a closed system where plants are grown under controlled hydroponic conditions. The plants in CELSS generate oxygen, purified water, and produce edible foods.

The CELSS resource recovery system, which is a waste processing system, uses aerobic and anaerobic bioreactors to recover plants nutrients and secondary foods from the inedible biomass. Studies have been carried out using aerobic and anaerobic bioreactors to recover plants nutrients and secondary foods from inedible crop residues. Crop residues contain significant amount of nitrate. There are actually two major problems concerning nitrate: 1) both CELSS biomass production and resource recovery consume large quantities of nitric acid, 2) nitrate causes a variety of problems in both aerobic and anaerobic bioreactors. Previous studies with aerobic biodegradation have experienced nitrogen losses through denitrification when low level of dissolved oxygen are reached due the rapid organic matter degradation. During the anaerobic biodegradation of inedible biomass, nitrate is converted to ammonia which reduces the system capacity to convert the organic matter to volatile fatty acids and needs further downstream processing steps to convert the ammonia back to nitrate. The nitrate anion causes several problems in the resource recovery system in such a way that, removal prior to the process is highly desirable.

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## ABBREVIATIONS, ACRONYMS AND NOMENCLATURE

BPC = Biomass Production Chamber  
CELSS = Controlled Ecological Life Support System  
ED = Electrodialysis

A = empirical constant  
 $A_m$  = effective membrane area,  $m^2$   
b = empirical number, dimensionless  
C = bulk solution ion concentration, Kg-equiv./ $m^3$   
 $C_0$  = boundary layer solution ion concentration, Kg-equiv./ $m^3$   
e = current efficiency, dimensionless  
F = Faraday's constant, 96,500 Coul./g-equiv.  
i = current density, A/ $m^2$   
 $i_{lim}$  = limiting current density, A/ $m^2$   
I = current, A  
 $J_e$  = ion flux by electrotransport, Kg-equiv./s- $m^2$   
 $J_D$  = ion flux by diffusion, Kg-equiv./s- $m^2$   
k = specific electrical conductivity, Mho/m  
 $N_f$  = diluate stream feed concentration, kg-equiv./ $m^3$   
 $N_p$  = diluate stream product concentration, kg-equiv./ $m^3$   
Q = volumetric flowrate,  $m^3/s$   
 $t_m$  = ion transport number in solution, dimensionless  
 $t_s$  = ion transport number in membrane, dimensionless  
U = linear fluid velocity, m/s  
  
 $\delta$  = boundary layer thickness, m

## I. INTRODUCTION

The National Aeronautical and Space Administration (NASA) has been studying the viability of Controlled Ecological Life Support System (CELSS) for long term space missions for several years. The purpose of this system is to provide all the basic human needs required for life support. The CELSS breadboard project is a large-scale integration system with two main components, a full-scale Biomass Production Chamber (BPC) and the Resource Recovery system. The BPC is a closed system where plants are grown under controlled hydroponic conditions. The plants in CELSS generate oxygen, purified water, and produce edible foods.

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### 1.1 BACKGROUND

Previous studies associated with the CELSS Breadboard project indicated that the water soluble extract of inedible biomass have been suitable for use as plant nutrient source in hydroponic systems (1,2). Water extraction or leaching, can be viewed as one step in an overall biological oxidation scheme (3), or as a pretreatment of biomass to remove nutrient prior to further treatment. Leaching was effective at removing the majority of nutrients from the inedible biomass (2). The aqueous leachate contains both inorganic and organic molecules. Biological pretreatment of leachate prior to its use in hydroponic systems have been recommended to both reduce phytotoxic effects and to convert soluble organic to edible products in regenerative systems (4). Based on the inorganic analyses of crop residues, leachate contains higher levels of nitrate and potassium when compared to others nutrients (5). Three Intermediate-Scale Aerobic Bioreactors have been designed, fabricated and operated (6). They utilized mixed microbial communities to bio-degrade plant residues. It was determined that the soluble organic compounds in the leachate were metabolized by microorganisms resident in the nutrient delivery system. It was found that this lead to increase total root respiration, the development of microbial biofilms on surfaces of roots and nutrient delivery system components, and increased denitrification (conversion of nitrate to nitrogen) by the rhyzosphere microbial community. It

was also observed that the aerobic decomposition of soluble organic compounds, the pH increased from 6.5 to 8.5. To control the pH during crop residues decomposition, a 1 N nitric acid solution was injected into the bioreactor.

Anaerobic digestion of inedible biomass is a natural occurring biological process in which organic material is converted to reduce end products. The anaerobic decomposition of solid organic wastes proceeds in two consecutive steps, liquification and methanogenesis (7,8). The first phase of the anaerobic digestion is known as the acidigenic phase (volatile fatty acids formation). In the second phase a second group of organisms, the methanogens, complete the digestion process converting the volatile fatty acids to highly reduced  $\text{CH}_4$  and  $\text{CO}_2$ . The presence of highly levels of nitrate in solution during the anaerobic decomposition of organic matter conducts to the undesired formation of ammonia. The aerobic dinitrification process consumes part of the medium dissolved oxygen, which is highly required to solubilize the organic matter present. The undesired anaerobic decomposition of nitrate to ammonia needs further nitrification process to convert back the ammonia to nitrate to be use as plant's nutrient.

Many researchers (9, 10, 11, 12) have described processes for producing weak acids from its salt via electrodialysis (ED), but do not address the process variables, e.g., the limiting current density, the membrane fouling effect, and hydrodynamic conditions on the solution-membrane mass transfer. Theoretical concepts and experimental research on the area of producing acids from its salts and desalination of saline water by electrodialysis gives better understanding of the process variables (9, 13, 14, 15, 16, 17). In a typical desalination system, the channels through which saline water passes are made of alternating cation and anion permselective membranes. The passage of a direct current through the stack of channels results in the depletion and enrichment of the salt in the alternating compartments. The rate of ion transfer is proportional to the current density. However, the current density at which the system can be operated is to a large extent limited by the polarization which take place in the dialysate channels. Polarization is a current saturation condition associated with a high ohmic resistance of the fluid because of the decreased ionic concentration. Theoretically, the limiting current is reached when the ionic concentration, which is lowest at the membrane surface, approaches zero. In practice, this is not attained because water ions themselves enter the transfer process. It has been long understood (13) that increasing the turbulence level in the fluid streams generally increases the limiting current by means of decreasing the fluid boundary layer thickness. This results from the increased rate of diffusion of ions towards the membrane surface to replenish those which have been depleted. It is normal to operate practical systems under turbulent conditions, through not excessively high Reynolds numbers, because of the associated higher pumping costs and inter-spacers leaking. In, practice, the Reynolds number may be low enough to indicate that the flow would be laminar, but turbulent promoters used result in a strong eddying motion.

Mass transfer through permselectives membranes consists of two steps:  
1) the reduction of ionic concentration in the solution by electrotransport of ions from the boundary layer near the membrane and 2) the diffusion of ions to the partially de-ionized boundary layer. The kinetics of the first step is given by the Nernst equation

$$J_e = (t_m - t_s)/(i F) \quad (1)$$

where  $J_e$  is the flux of ions by electrotransport,  $I$  is the current density,  $F$  is the Faraday's number,  $t_s$  is the ion transport number in solution, and  $t_m$  is the ion transport number on membrane. The second step is given by the Fick's first law:

$$J_D = D(C-C_0)/\delta \quad (2)$$

where  $J_D$  is the flux of ions by diffusion,  $D$  the diffusion coefficient,  $C$  the ion concentration of bulk solution,  $C_0$  the ion concentration at the boundary layer, and  $\delta$  the thickness of the boundary layer. The thickness of the boundary layer is a function of the fluid velocity and geometry of the spacers (18). From the equations (1) and (2), the following can be derived:

$$i = DF(C-C_0)/\delta(t_m - t_s) \quad (3)$$

Increasing the voltage of the stack raises the current density. The flux of ions by electrotransport is also increased until the concentration of the solution boundary layer approaches zero ( $C_0 = 0$ ). Under these conditions the flux of ions by diffusion is maximal; therefore, the current density is the limiting one ( $i = i_{lim}$ )

$$i_{lim} = DFC/\delta(t_m - t_s) \quad (4)$$

A further increase in  $J_D$  can be achieved only by raising the fluid velocity of the solution in the cell to a level at which the pressure drop across the cell will not cause internal leakage. A further increase in the stack voltage will raise the current density. Most of this additional current will cause dissociation of water rather than mass transfer from the diluate cell compartment. When the concentration of the solution in the boundary layer decreases, the electrical resistance of cell diluate solution increases. Therefore, it is important that the current density be prevented from approaching the limiting current-density value. A practical equation for limiting current density, derived from empirical results and suggested by several authors (19,20) is

$$i_{lim}/k = AU^b \quad (5)$$

where  $U$  is the fluid velocity,  $A$  is an empirical constant number,  $b$  is an empirical number, generally between 0.5 to 0.9, and  $k$  is diluate solution average specific electrical conductivity.

Material balances over the membrane area across the diluate solution is flowing through,

and in which a direct current is being passed, the following equation can be obtained for an electrolytic cell continuous mode of operation (9):

$$\ln \frac{N_f}{N_p} = \left[ \left( \frac{e}{F} \right) \left( \frac{i}{N_d} \right) \left( \frac{A_m}{Q} \right) \right] \quad (6)$$

From an empirically determined relationship between  $(I/N_d)$  and the fluid velocity, values of  $(I/N_d)$  and  $A_m$  may be chosen. For batch recirculation electrolytic cell mode of operation, it is apparent that multiple passes through a single stack are equivalent as to passing the solution through several stacks in series. The performance equation for a batch recirculation process is as follows:

$$\frac{N_f}{N_{pn}} = \exp \left( \frac{A_m}{FQ} \sum_{k=1}^n \left( \frac{i}{N_d} \right)_k e_k \right) \quad (7)$$

If the process is carried out at constant average value of  $(I/N_d)_{AV}$  and assuming an average current efficiency,  $e_{av}$ , Eq. 7 can be simplified to:

$$\ln \frac{N_f}{N_{pn}} = \left( \frac{ne_{av}}{F} \right) \left( \frac{i}{N_d} \right)_{av} \left( \frac{A_m}{Q} \right) \quad (8)$$

The value of  $(I/N_d)_{av}$  may be simulated partially by operating at a constant voltage determined empirically from polarization studies.

Permselective membranes for electrodialysis (ED) contain either group of positive ions (anion-exchange membrane) or negative ions (cation-exchange membrane). In an applied electric field and in aqueous solution of ions, an anion-exchange membrane permits the passage of anions; a cation-exchange membrane permits the passage of cations only. The most important characteristics of permselective membranes used for ED are: low electrical resistance, good permselective qualities for cations and anions, good mechanical stability, and high chemical stability. A nitrate-specific anion-exchange membrane was prepared from chloromethylated polysulfone by partially aminating it with a secondary amine for completion (21). When the nitrate-chloride ratio in solution was equal, nitrate flux was larger than chloride by a factor of 1.6 in alkaline medium and a factor of 2 in acid medium.

## 1.2 PROPOSED TECHNOLOGY

The technique proposed to remove the nitrate from potato inedible biomass leachate and

to satisfy the nitric acid demand is a four compartment electrolytic cell (see Fig. 1). This cell contains two cation and one anion permselective membranes for defining the cell compartments. The compartments are separate by means of polypropylene tortuous spacers which contains turbulent promoters to enhance the mass transfer from the bulk solution to the membrane surface, where the separation is carried out, thus permitting the cell to operate at a high current density. When an electrical potential is applied to the electrolytic cell by mean of a power supply, potassium ions and other cations move to the cathode while nitrate ions and other anions move to the anode. At the cathode compartment potassium ions are combined with hydroxide ions product of water electrolysis to produce potassium hydroxide. The electrolytic reduction of water also produces hydrogen gas which may be used as a potential fuel. The nitrate ions removed from the leachate compartment pass through the anion-exchange membrane to the nitric acid compartment and combine with the hydrogen ions that come from the anode compartment to enrich the nitric acid solution. At the anode compartment water oxidizes under acid conditions and produces oxygen gas and hydrogen ions. Oxygen gas may be use to satisfy any human being needs, as well as, to be combined with hydrogen gas for energy purposes.

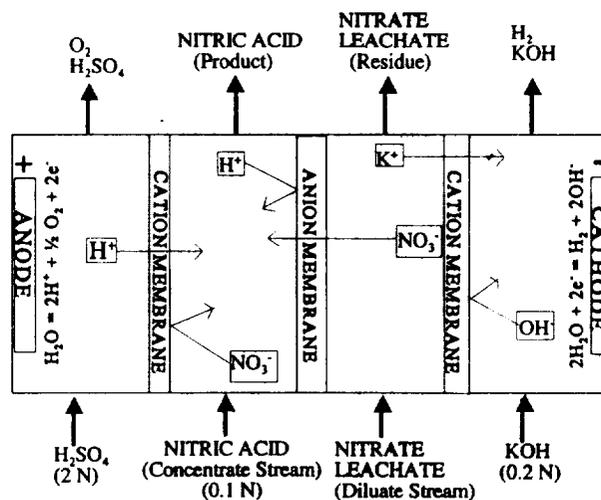


Fig. 1. Configuration of Electrolytic Cell

### 1.3 OBJECTIVES

The main objective of this summer project was to design, and test an electrolytic system to remove nitrate from crop residues, as well as, to satisfy biomass production chamber (BPC) and anaerobic and aerobic nitric acid demand. The potato crop residues was leached and the resultant leachate electrolyzed to remove nitrate. In the design of this process, variables such as current density, applied voltage, fluid hydrodynamic conditions and leachate ionic concentration were correlated to optimize nitrate removal.

## II. EXPERIMENTAL SET-UP

### 2.1 ELECTROLYTIC CELL

The experimental system consists of a 0.23 x 0.25 m four compartments electrolytic cell (Fig. 2). The electrodes are a stainless steel cathode and a titanium substrate plated anode. The membranes selected were two heavy duty cation permselective membranes (Type 61-AZL-389, from IONICS, Inc., Watertown, MA) and one anion permselective membrane (Type 103-QZL-386, from IONICS, Inc., Watertown, MA). The separation between electrodes and cation membranes and between membranes were done with polypropylene tortuous path spacers that contain the channeling and turbulent promoters. The thickness of electrodes spacers is  $2 \times 10^{-3}$  m and the intermembrane spacer is  $1 \times 10^{-3}$  m. The open flow area is  $6 \times 10^{-6}$  m<sup>2</sup> for intermembrane compartments and  $1.2 \times 10^{-5}$  for electrodes compartments. The effective membrane area is 0.023 m<sup>2</sup>.

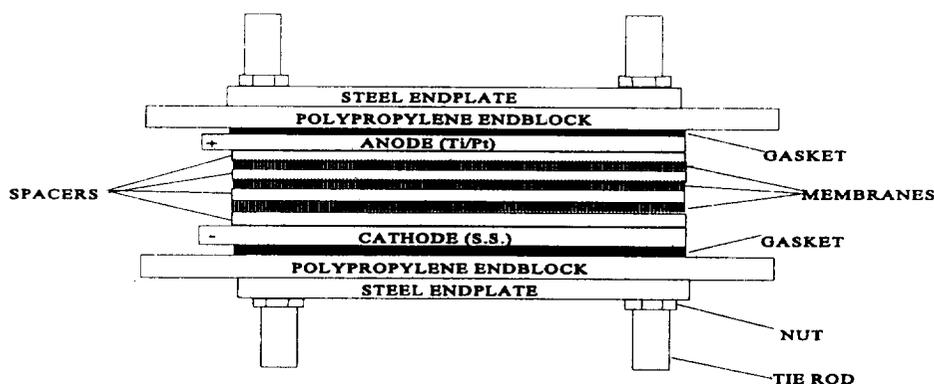


Fig. 2. Four Compartments Electrolytic Cell Construction

### 2.2 COMPARTMENTS SOLUTIONS AND HYDRODYNAMIC CONDITIONS

The cathode compartment feed solution was a 0.2 N KOH. The solution feed to the compartment next to the cathode was a filtered potato leachate. The specific protocol for leaching potato inedible ground biomass is elsewhere (1). An overview of the relevant conditions were as follows: 1) loading rate of 50 g of biomass per liter of deionized water, 2) duration time of 2 hr, 3) aeration rate of 20 LPM, and 4) rising with an equal volume of deionized water in five separate washings. Then the leachate was filtered with a 200  $\mu$ m stainless-steel wire mesh to remove the suspended matter that may clog the electrolytic cell flow channel. The composition of the leachate obtained by the previously mentioned method is shown

in Table 1. The nitric acid feed solution was a 0.1 N HNO<sub>3</sub> and the anode feed solution was a 2 N H<sub>2</sub>SO<sub>4</sub>. The nitric acid and potassium hydroxide solutions were prepared in such a way, to keep the ratio of the specific electrical conductivities of these solutions to the leachate solution below 10 to prevent back diffusion and thus to avoid short circuit through the manifold ( $k_{\text{HNO}_3}/k_{\text{Leachate}} = 3.4$ ,  $k_{\text{KOH}}/k_{\text{Leachate}} = 4.2$ ). The fluids velocities flowing through the tortous spacers were varied from 0.083 to 0.403 m/s given Reynold's numbers (based on the equivalent hydraulic diameter of  $1.714 \times 10^{-3}$  m) of 142 to 691. The flowrates through the electrodes compartments were doubled as compared to the leachate and nitric acid solutions which kept the same fluid velocity.

Table 1. Potato Leachate Average Composition

| Analysis                        | Composition |
|---------------------------------|-------------|
| Spec. Cond., $\mu\text{Mho/cm}$ | 8650        |
| pH                              | 5.81        |
| NO <sub>3</sub> , mg/L          | 1474        |
| PO <sub>4</sub> , mg/L          | 154         |
| K, mg/L                         | 2877        |
| Ca, mg/L                        | 7.5         |
| Mn, mg/L                        | 157.1       |
| Fe, mg/L                        | 4.26        |
| Cu, mg/L                        | 0.16        |
| Mg, mg/L                        | 0.95        |
| Zn, mg/L                        | 0.75        |
| NH <sub>4</sub>                 | 56.9        |
| Cl, mg/L                        | 70.4        |
| TOC, mg/L                       | 3039.8      |

### 2.3 LIMITING CURRENT DETERMINATION

The determination of the limiting current density (maximum operating current density) was carried out by operating the system with the respective solutions under continuous operation mode. A pH electrode, a specific electrical conductivity flow cell, and thermocouples were

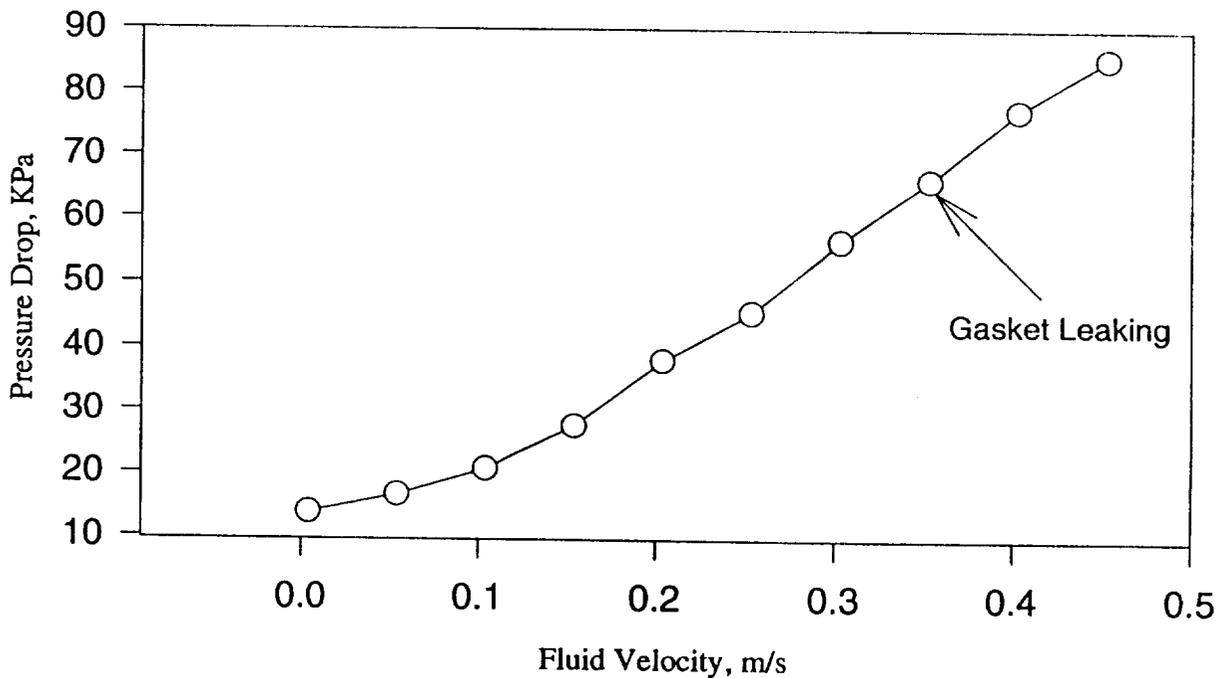
installed at the outlet of the potato leachate stream to monitor pH, specific electrical conductivity, and temperature difference, respectively, as a function the applied current density and hydrodynamic conditions. Also the applied voltage vs current density was monitored to determine the cell electrical resistance.

### III. RESULTS AND DISCUSSION

#### 3.1 ELECTROLYTIC CELL PRESSURE DROP

The electrolytic cell was tested for external leakage by pumping de-ionized water at room temperature through each compartment at the same fluid velocity. As can be observed in Fig. 3., the pressure drop through the electrolytic cell increases rapidly with fluid linear velocity (flowrate). At fluid velocities higher than 0.35 m/s external leakage was observed between spacer-membrane junction. Thus, the maximum permissible flowrate is limited by high pressure drop and external leakage. At a fluid velocity of 0.35 m/s, in which the external leakage began the pressure drop, was approximately 66.2 kPa (9.6 psi). Therefore, it is also more economical to operate below the maximum allowable pressure of 66.2 kPa.

Fig. 3. Electrolytic Cell Pressure Drop with Fluid Velocity



#### 3.2 POLARIZATION (LIMITING CURRENT DENSITY)

“Current density” in general is defined as the current per unit area of available membrane through which the current passes. The effective membrane area of the electrolytic cell is of 0.023 m<sup>2</sup> (230 cm<sup>2</sup>). In solution electrical current is carried by ions, it is follow that more dilute the solution the lower will be the current transmittal capacity of the solution. Application of too

much voltage will result in ion starvation at the membrane-solution interface with the resultant decomposition of solvent and/or other materials that may be present. This phenomenon is referred to as polarization and manifest itself through pH disturbances in solution, increase in electrical resistance, and loss of current efficiency. Consequently, the limiting current density is the first operating variable that should be established experimentally.

Fig. 4. shows the applied voltage vs current relationship for the operation of the electrolytic cell under continuous mode of operation at different fluid velocities ranging from 0.083 to 0.403 m/s. From the Ohm's law ( $E = IR$ ), the slope of the voltage-current relationship at a given current is the cell electrical resistance. As can be observed in this figure the slope (cell electrical resistance) is small at low current, but as current is increased there is current where it suddenly changes from a finite value to almost infinity. The current at which this drastical change occur is known as the maximum permissible current or limiting current. The limiting current increases with increasing fluid velocity. As the fluid velocity is increased, the boundary layer thickness decreases, thus higher permissible current can be used. The effect of increased flow velocity included the enhancement of mass transfer, reduction of membrane fouling, and therefore minimization of polarization. The average cell electrical resistance is approximately 2 ohms when the operation is carried out below limiting current conditions. When the cell electrical resistance increases drastically some of the energy required to transport ions, dissipates as heat due to the Joule heating effect (see Fig 5). Thus, this effect increases the fluid temperature as it passes through the cell. It is suggested to operate at low temperature as possible to avoid membrane overheating and thus, to maintain the chemical stability of the permselective membranes for long period of operation. Most of the commercial polymeric-basis membranes can be used for an extended period at a temperature up to 40°C, warmer operation entails a great reduction of useful life. As can be observed in Fig. 6, the operation at current density higher than the limiting one produce pH disturbances in the leachate stream, as well as, loss of current density (leachate specific electrical conductivity is independent of current density). Thus, the operation at current density higher than the limiting one will may result in decomposition of solvent and other materials presented in the leachate. As the fluid velocity increases the pH disturbances and loss of current efficiency are minimized by increasing the mass transfer of ions from the solution bulk to the membrane interface. Fig. 7, shows the limiting current density as a function of leachate fluid velocity. These data were correlated very well by the power function model:  $i_{lim} = 576.41 U^{0.667}$ . The resulting correlation coefficient obtained is 0.995. This correlation agrees with the one suggested by several authors (19,20). Once the limiting current density is known at a given fluid velocity, selection of operating current density below the limiting one will warranty an optimum electrolytic cell performance. Due to the fluid velocities range used (laminar flow conditions), the tortous path flow channels through which the solution is passing appear to function as causing a degree of localized eddying rather than inducing turbulence flow.

Fig. 4. Electrolytic Cell Applied Voltage vs Current at Different Fluid Velocities

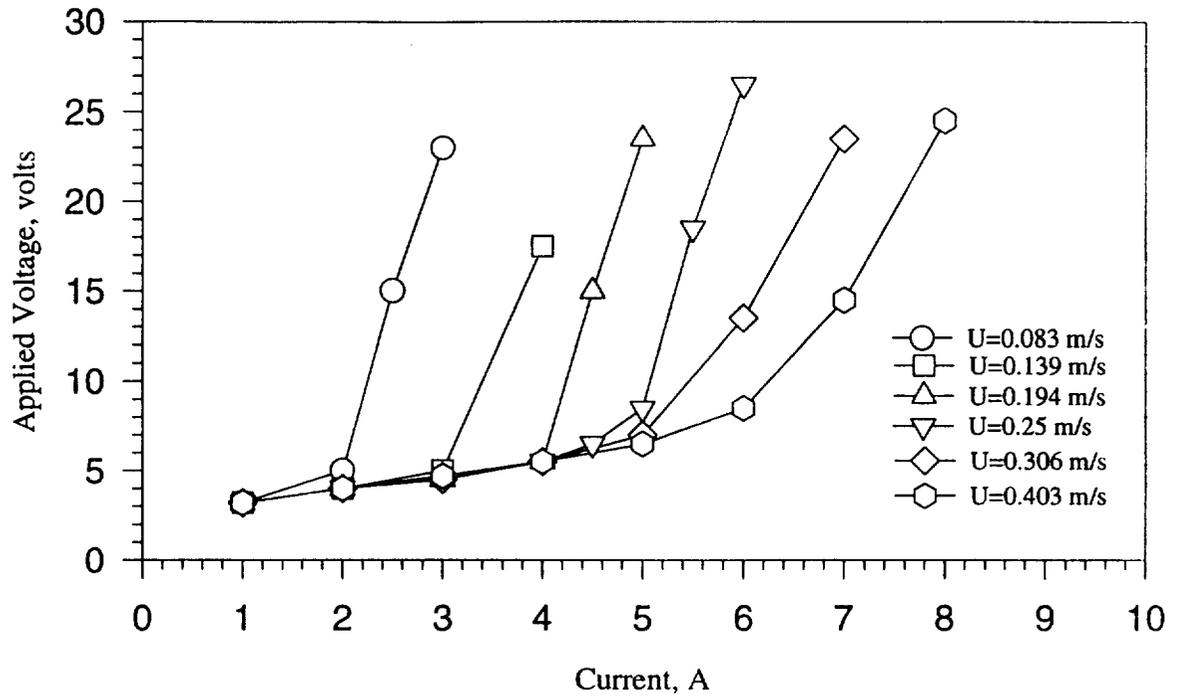


Fig. 5. Leachate Temperature Change Through the Electrolytic Cell as Function of Fluid Velocity and Applied Current

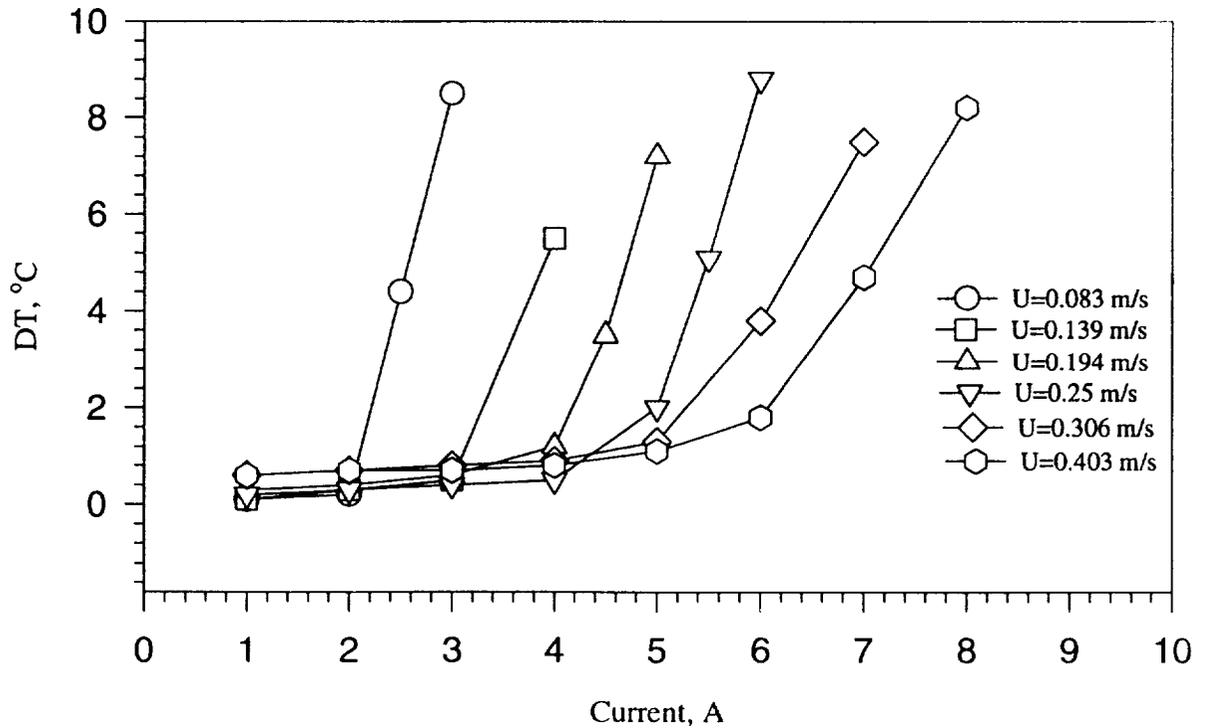


Fig. 6. Leachate Effluent Specific Electrical Conductivity and pH vs Current Density during Once-Through Continuous Operation

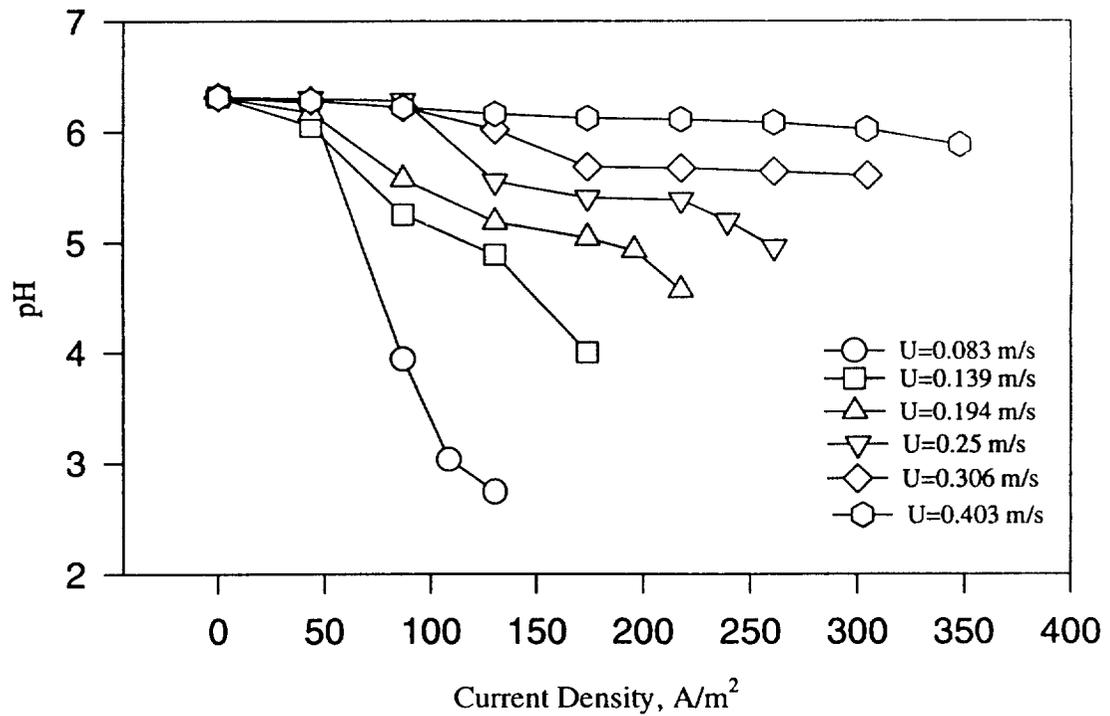
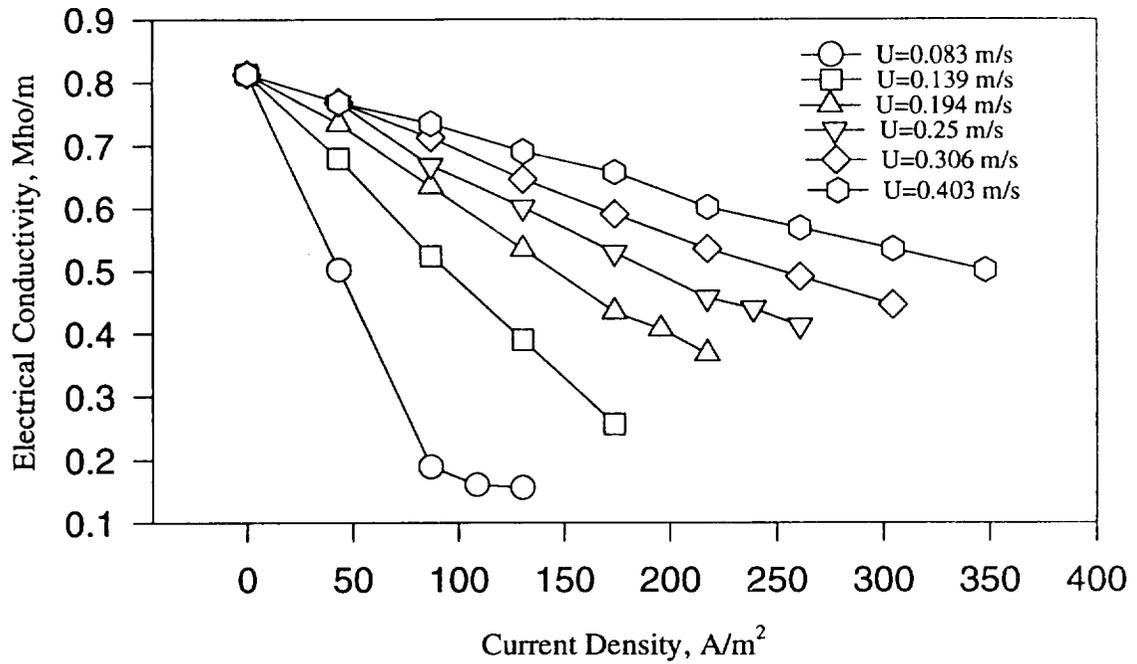
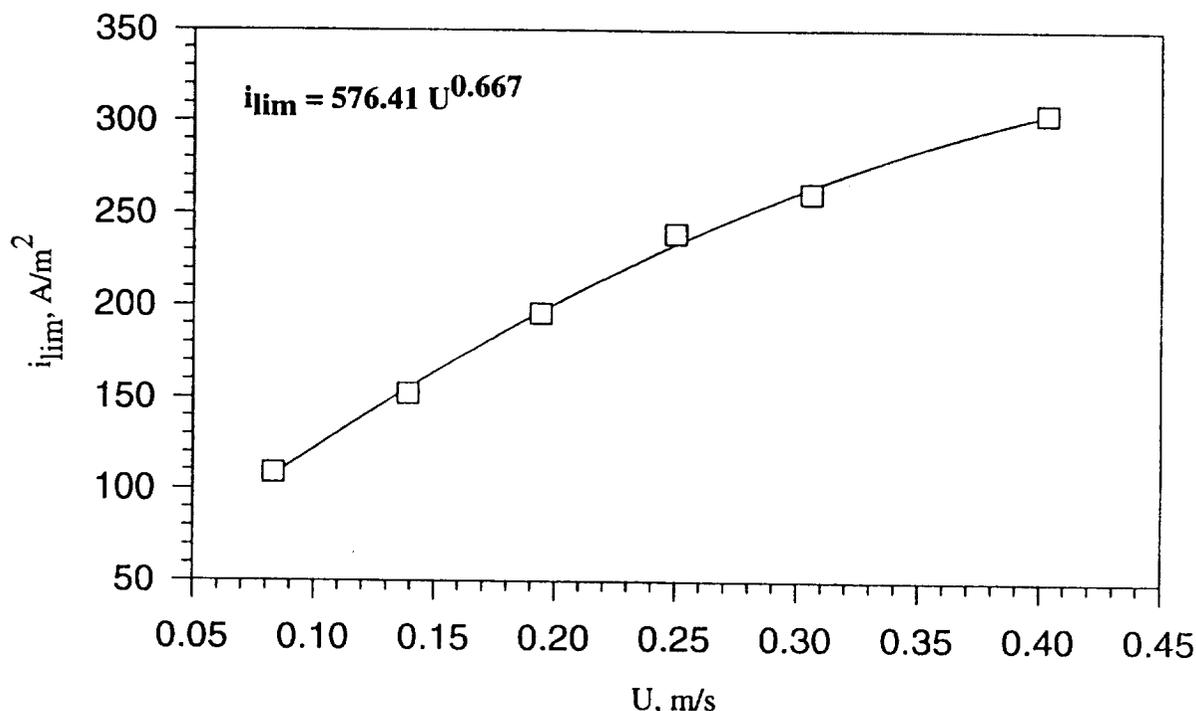


Fig. 7. Effect of Fluid Velocity on Electrolytic Cell Limiting Current Density



### 3.3 ONCE-THROUGH CONTINUOUS OPERATION

This operation was carried by pumping the solutions once through the electrolytic cell from feed tanks at a constant flowrate. As the diluting stream (leachate solution) passes through, the electrolytic cell becomes more demineralized. The concentrating stream (nitric acid solution) becomes more concentrated. In a continuous (once-through) operation the solution to be processed was passed through the electrolytic cell only once. This is convenient when one "pass" suffices to achieve the desired degree of demineralization.

Fig. 8 shows the leachate demineralization as a function of current density at a fluid velocity of 0.083 m/s. As can be seen, the removal per pass of each nutrient contained in the potato leachate increased with current density. The removal of nitrate, potassium, and chloride ions are much higher than the other ions present. At low current density of 44  $A/m^2$  is possible to remove up to 62.6% nitrate, 40.3% potassium, 26.5% chloride, 33.7% magnesium, 30.6% manganese, 38.2% zinc, 9.41% iron, and 19.8% phosphate, respectively. Although the removal of nutrients from potato leachate increase with current density, operation at current density higher

than  $108.7 \text{ A/m}^2$  (limiting current density) is not recommended due to excessive solution and membrane overheating. Operation at the limiting current density condition is possible to remove up to 92% nitrate, 92.5% potassium, 22.1% phosphate, 39.8% calcium, 71.4% magnesium, 39.9% iron, 42.3% zinc, 56.7% manganese and 92.4% chloride. The removal of monovalent ions was found to be higher than divalent ions because monovalent ions have higher mobility (current transmittal capacity) than divalent ones. At current density higher than the limiting one the removal of ions is almost independent of current density. At these conditions a big portion of electrical energy is being spent to heat the solutions (joule heating effect). As the fluid velocity is increased, the fluid residence time in the electrolytic cell decreases; therefore, lower demineralization per pass is obtained (see Figure 9 and 10). Increasing the fluid velocity will permit the operation at higher current density with minimum polarization, fouling, and solution and membrane overheating. At a fluid velocity of  $0.25 \text{ m/s}$  and operating at the lower current density of  $43.8 \text{ A/m}^2$  is possible to remove 12.4% nitrate, 6.2% potassium, 9.8% phosphate, 23.5% calcium, 9% magnesium, 6.4% iron, 10.4% zinc, 6.9% manganese, and 15.7% chloride, respectively. While the operation at the limiting current density ( $239.13 \text{ A/m}^2$ ) makes possible to remove up to 74.7% nitrate and 46% potassium; the operation at fluid velocity of  $0.306 \text{ m/s}$  and limiting current density ( $260.9 \text{ A/m}^2$ ) makes possible to remove up to 43.6% nitrate and 40.1% potassium (see Fig 10). It is recommended to operate the electrolytic cell process at fluid velocities between  $0.20$  to  $0.25 \text{ m/s}$  and current densities from  $200$  to  $225 \text{ A/m}^2$ . Operation at these conditions minimize solution and membrane overheating, as well as, polarization and membrane fouling effects.

### 3.4. BATCH-RECIRCULATION OPERATION

In batch-recirculation operation of the electrolytic cell system, the solutions to be processed were placed in their respective reservoir tanks. They were passed through the stack and then recycled back to the reservoirs. Thus, the leachate solution became increasingly depleted while the nitric acid solution became more concentrated. The electrolytic process was considered complete when the nitrate content drop to desired degree.

Batch operation has the advantage that the process cycle can be geared toward the desired end product and is relatively independent of the feed, the concentration of which may vary from batch to batch. Even if the feed varies, batch recirculation is equivalent to operate a number of electrolytic cell stack in series, with each stack receiving an increasingly depleted nitrate solution and concentrated nitric acid solution feed.

There are two ways to operated the electrolytic cell under batch-recirculation mode of operation, at constant-current and at constant-applied-voltage. The operation at constant-current would seem attractive for assuring a constant rate of nitrate removal from potato leachate, but this will be true only if the feed composition remain constant. One alternative is to operate so that the cell current is constant and below the value of the initial limiting current. For part of the process duration, the operating current lies below the limiting one, and this represents an under-utilization of the system capacity. When the operating current exceeds the limiting one,

Fig. 8. Removal of Selected Nutrients from Potato Leachate vs Current Density at  $U = 0.083$  m/s

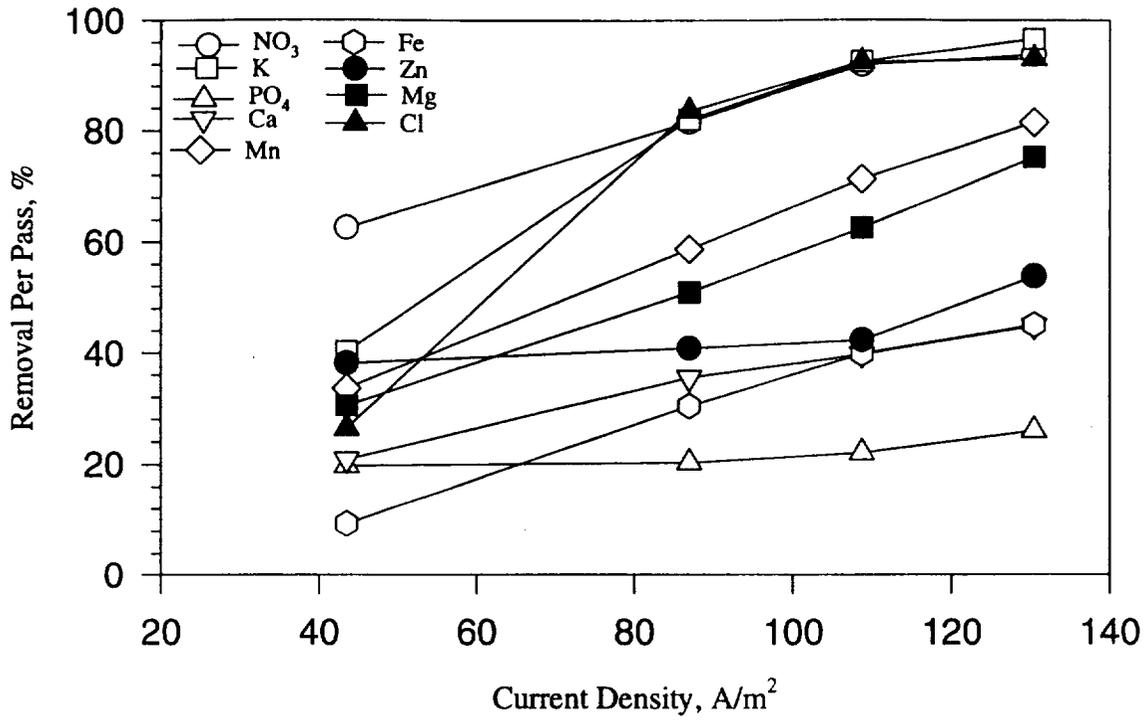
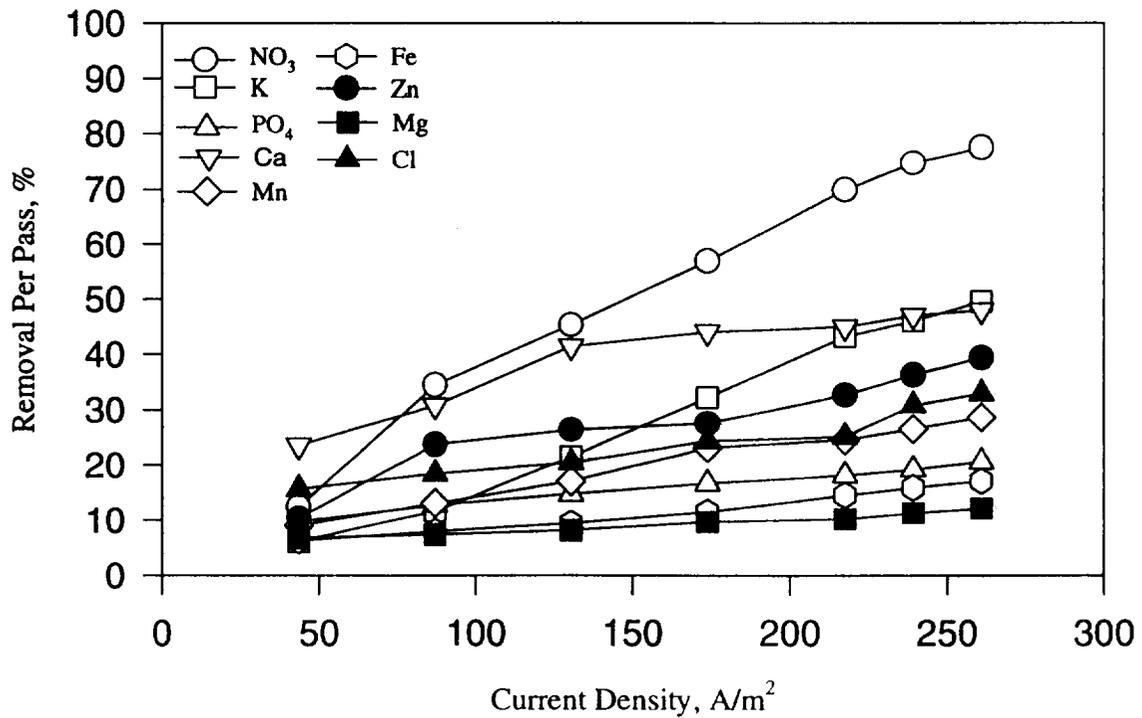


Fig. 9. Removal of Selected Nutrients from Potato Leachate vs Current Density at  $U = 0.25$  m/s



secondary reactions begin, resulting in power wastage. Therefore, constant current operation is impractical for use with batch-recirculation systems, which would be operated over a wide ionic concentration range. This realization leads to the concept of using high current levels during the initial part of the process and reduced levels when the ionic concentration of the leachate falls. One way of accomplishing this, is to switch to a constant applied voltage operation. The operation was carried out in two trials at constant applied voltages of 4.5 and 8.5 volts, respectively. The reservoir tanks were charged with 2 liters of each solution. The flowrate was adjusted to give a fluid velocity of 0.25 m/s for all the trials.

Fig. 10. Removal of Selected Nutrients from Potato Leachate vs Current Density at  $U = 0.306$  m/s

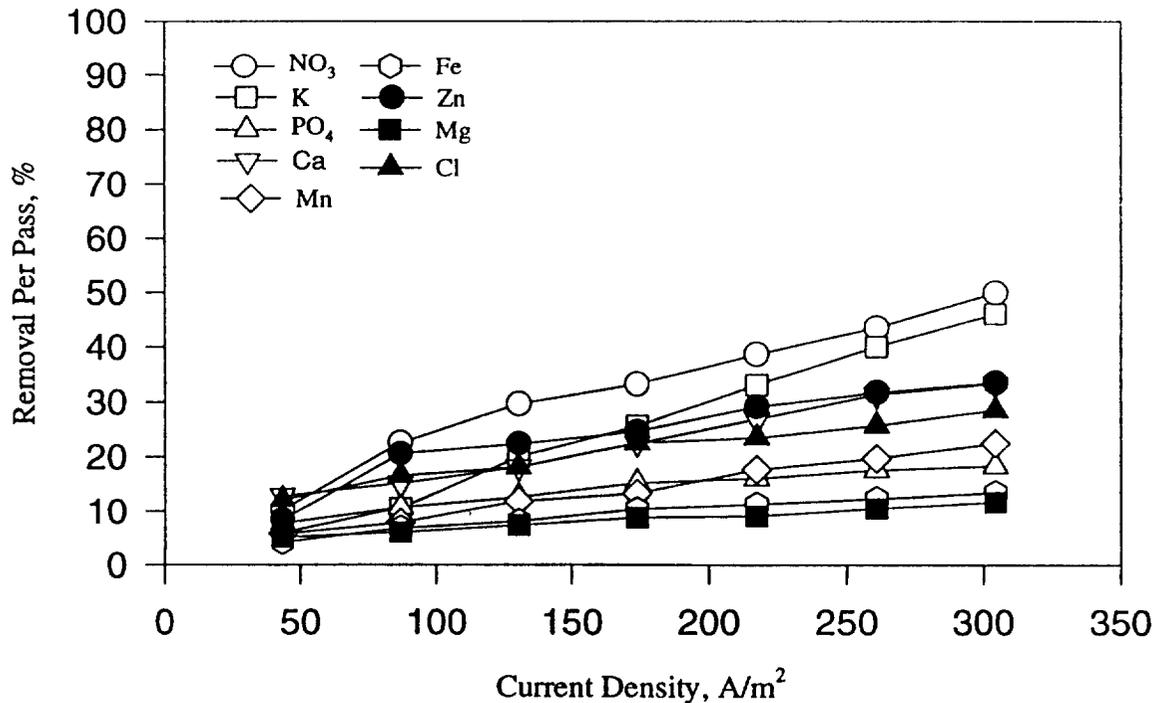


Fig. 11 shows the current density versus time relationship for the batch-recirculation operation at constant applied voltage conditions. At a constant applied voltage of 8.5 volts, the current density declines rapidly during first the 20 minutes, and then levels off with a diminishing rate for the remaining period of time. This occurred as consequence of a rapid demineralization of the leachate at high current density. As the ionic concentration of the leachate diminishes, the solution electrical resistance increases rapidly, thus to keep the same applied voltage, the current density is itself adjusted to lower values. The operation at constant applied voltage of 4.5 volts, required lower initial current density, thus the initial rate of demineralization was low enough to

keep small variation of solution electrical resistance. After the period of 20 minutes of operation the patterns of current density variation vs time at both applied voltages were very similar. This means that the rate of demineralization is slow at low current density. As can be observed in Fig. 12, the specific electrical conductivity versus time at both applied voltages have a similar pattern. The leachate solution electrical conductivity decreases with operating time as the leachate solution is depleted. Also, as being seen in Fig. 13, the leachate solution pH decreases slowly from 5.8 to 4.2 at  $E = 8.5$  volts and from 5.7 to 4.53 at  $E = 4.5$  volts. At a low applied voltage ( $E = 4.5$  volts), pH is more stable than at high applied voltage ( $E = 8.5$  volts), which means a low degree of water de-ionization or low polarization effect.

Figures 14 and 15 show the demineralization of potato leachate as function of time. The initial rate of demineralization is high and then levels off. The initial rate of demineralization is higher for two reasons; initially the leachate solution contains a high concentration of ionic species and the initial current density is also high. As the leachate become more depleted, both current density and the rate of nutrient removal decrease. The average rate of nutrient removal was almost independent of applied voltages, but depends on operating time. During the operation of the electrolytic cell at constant applied voltage of 4.5 volts for 158 minutes, made possible to remove up to 92.1% nitrate, 26.5% phosphate, 79.2% potassium, 39.2% calcium, 68.2% magnesium, 38.5% iron, 38.8% copper, 48.2% manganese, 44% zinc, 88.7% chloride, and 22.7% TOC, respectively. Approximately the same overall removal was obtained when the system was operated at constant applied voltage of 8.5 volts, but for a period of 148 min. As the cations are transferred to the cathode compartment, the alkali concentration increases with time (see Fig. 16). The concentration of alkali solution was found to change from 0.209 to 0.266 N for the operation at 4.5 volts (27.3% conversion) and from 0.201 to 0.257 N at 8.5 volts (27.9% conversion). The alkali formation is the product of the electrochemical reaction at the cathode surface that produces hydroxide ions which are combined with the cations to form alkali compounds. Also, as the anions are transferred to the nitric acid compartment, the acid concentration was found to increase with time. The concentration of the acid solution in the nitric acid compartment was found to increase from 0.098 to 0.151 N for the operation at 4.5 volts (54.1% conversion) and from 0.098 to 0.152 at 8.5 volts (55.1% conversion). From material balances was found that the average oxygen gas ( $O_2$ ) produced at the anode surface under acid condition was approximately 2.2 moles  $O_2$ /mole  $NO_3$  transferred. The average production of hydrogen gas at the cathode surface was found to be approximately 4.4 moles  $H_2$ /mole  $NO_3$  transferred.

Fig. 11. Current density vs Time during Batch-Recirculation Operation at Constant Applied Voltages and  $U = 0.253$  m/s

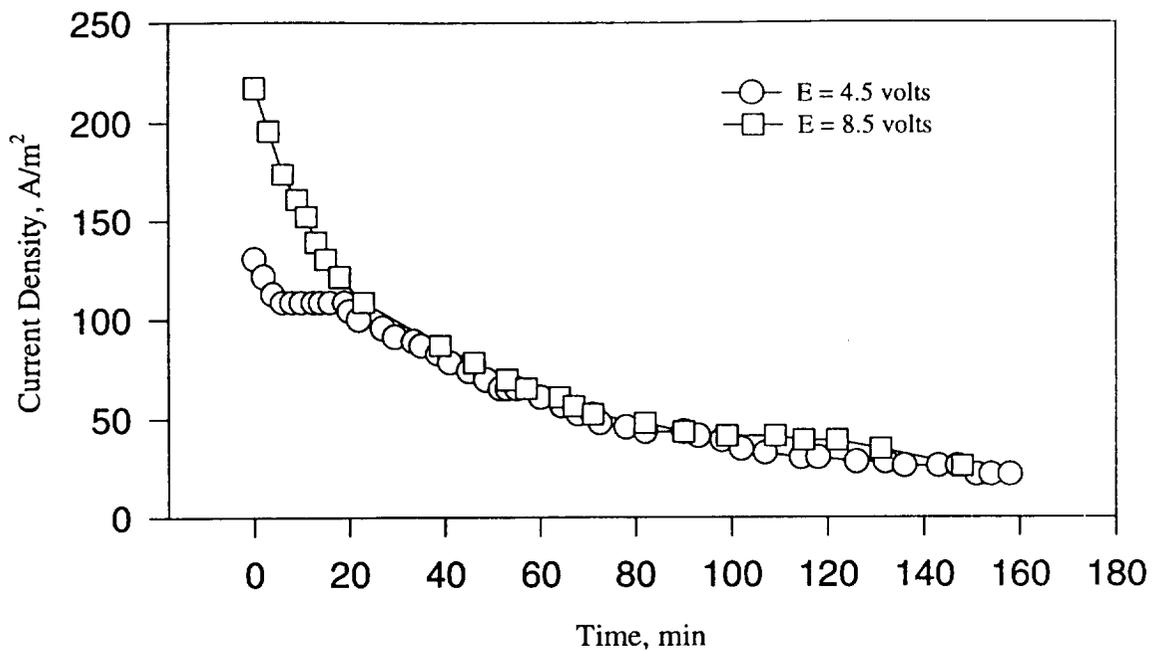


Fig. 12. Leachate Specific Electrical Conductivity vs Time during Batch-Recirculation Operation at Constant Applied Voltages and  $U = 0.253$  m/s

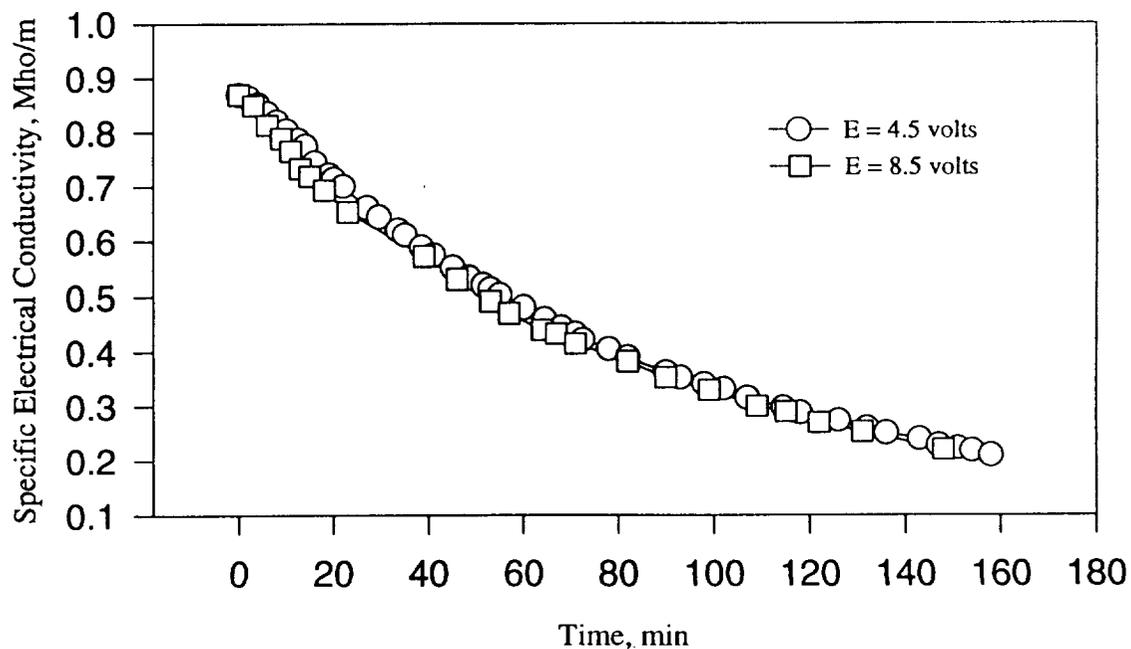


Fig. 13. Leachate Solution pH during Batch-Recirculation Operation at Constant Applied Voltages and  $U = 0.253$  m/s

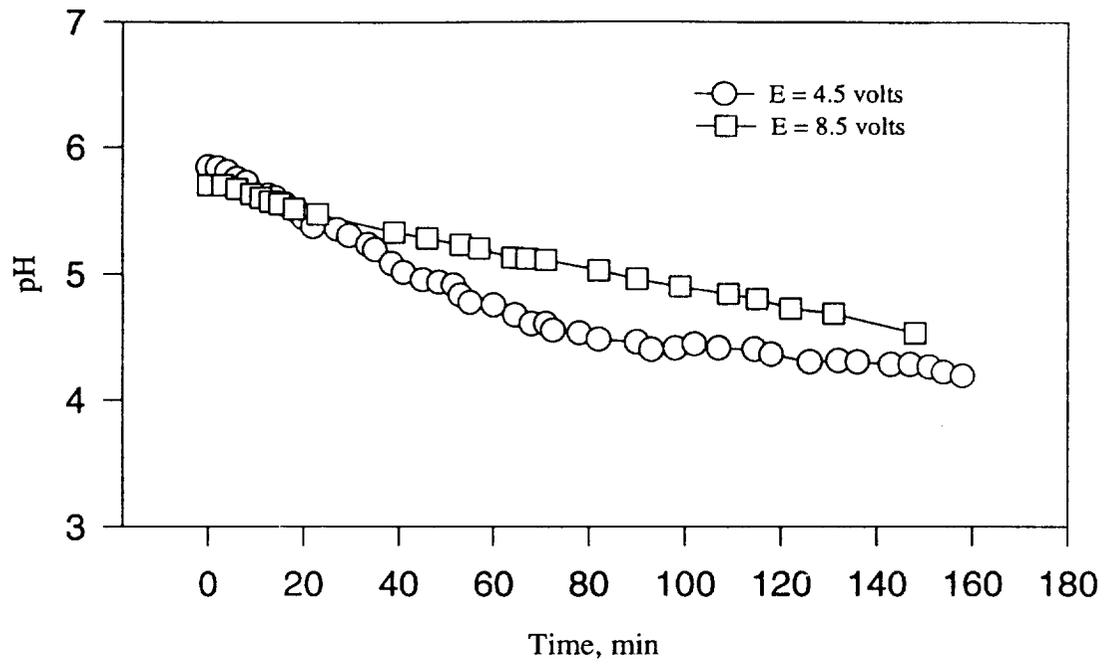


Fig. 14. Nutrient Removal during Batch-Recirculation Operation at  $E = 4.5$  volts and  $U = 0.253$  m/s

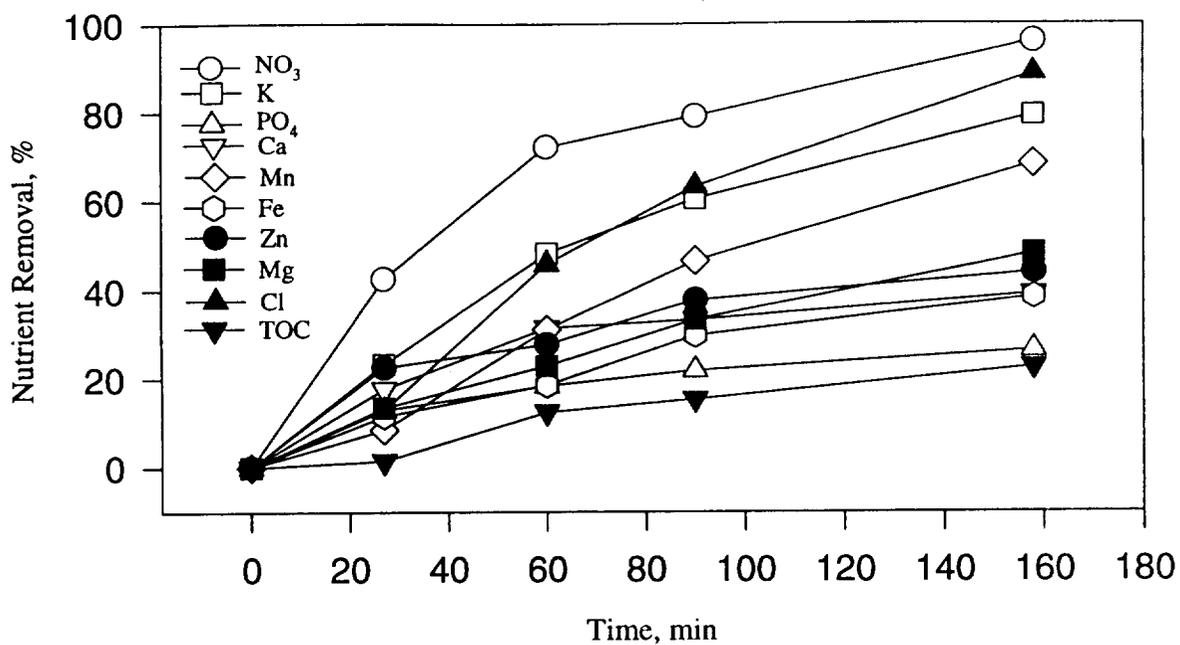


Fig. 15. Nutrient Removal during Batch-Recirculation Operation at  $E = 8.5$  volts and  $U = 0.253$  m/s

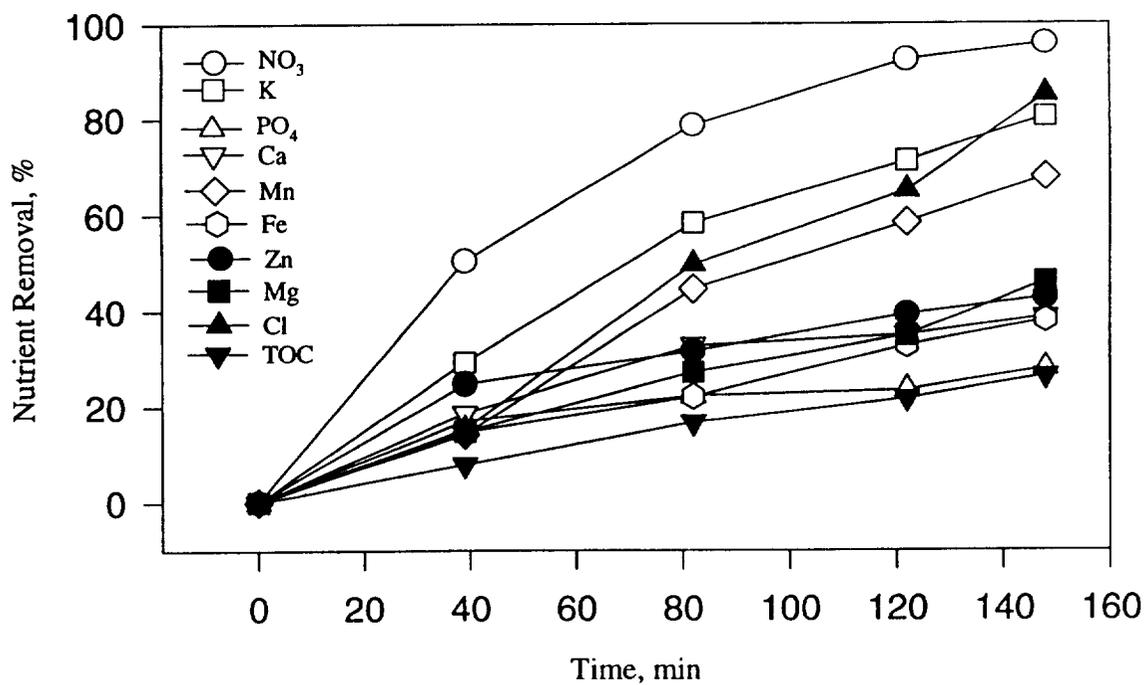
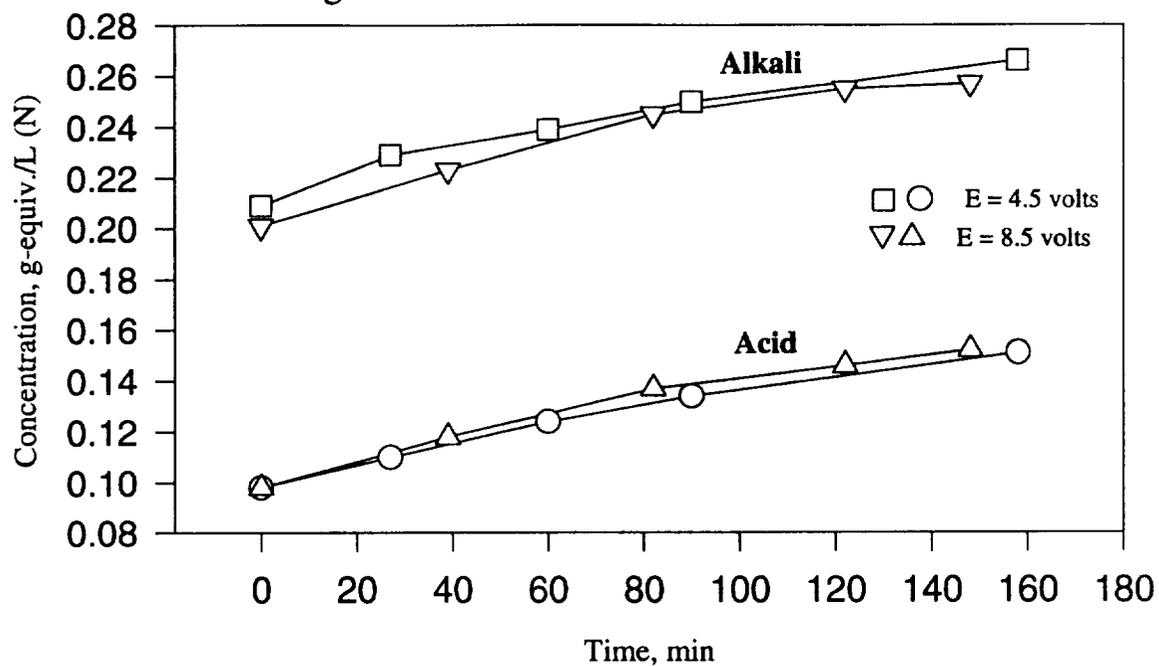


Fig. 16. Nitric Acid and Potassium Hydroxide Concentration vs Time during Batch-Recirculation Operation at Constant Applied Voltages and  $U = 0.253$  m/s



#### IV. CONCLUSIONS

The limiting current density (maximum operating current density) was found to be directly proportional the solution electrical conductivity an a power function of the linear fluid velocity in the range between 0.083 to 0.403 m/s. The operation at current density higher than the limiting one, results in pH disturbances which may decomposes pH sensitive leachate components, excessive solution and membrane overheating, which may reduce membrane useful life , and loss of process current efficiency.

During the electrolytic cell once-through operation, the nitrate, potassium, and other nutrients removal rates were proportional to current density and inversely proportional to fluid velocity. Although the removal of nutrients from potato leachate increase with current density, operation at current density higher than the limiting one is not recommended due to excessive solution and membrane overheating. The removal of monovalent ions was found to be higher than divalent ones, because monovalent ions have higher mobility in solution, as well as, are more membrane selective than divalent ones. The operation at high fluid velocities reduced the ion removal capacity per pass, but increases bulk solution-membrane interface mass transfer, which reduces membrane fouling to extent membrane useful life

Under batch-recirculation operation at constant applied voltage of 4.5 and 8.5 volts, it was found that the nutrient removal rates were independent of applied voltage, but proportional to the ions concentration and operating time. The initial nutrients removal rates were found to be high because of the high initial solution ionic concentration and current density. This operation appeared to work as a current self-regulating process, because as the leachate becomes depleted the solution electrical resistance increases, therefore to maintain the constant applied voltage condition the current is self adjusted to lower values. From material balances it was found that 2.2 moles of oxygen gas and 4.4 moles of hydrogen gas were produced at the electrodes surfaces per mole of nitrate transferred.

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